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(54) Title: PROCESS FOR PREPARING BUBBLE-FREE ADHESIVE COMPOSITIONS (57) Abstract Light transparent, visible bubble-free, curable adhesive compositions, their method of manufacture and their use in producing optically brilliant three-dimensional signs for both interior and exterior use are disclosed. The compositions include acrylate-based UV light curable monomers and oligomers and moisture curable room temperature vulcanizing silicones, optionally comprising UV stabilizers. The compositions may contain dispersed pigments and are made by low shear mixing, such as static mixing or rolling, optionally, followed by spinning to remove visible air bubbles.		

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**PROCESS FOR PREPARING BUBBLE-FREE
ADHESIVE COMPOSITIONS**

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FIELD OF THE INVENTION

15 This invention relates to curable, bubble-free adhesive compositions, particularly curable acrylic and silicone compositions; to the preparation of said bubble free compositions; to the use of said compositions in the manufacture of illuminated signs; and to such signs comprising cured said bubble-free compositions.

BACKGROUND TO THE INVENTION

20 As is well-known, illuminated signs have long been made by sealing neon, or other suitable inert gas, in a low-pressure tube through which electricity is passed. This causes the neon to "glow" and if the tube is shaped appropriately, a "neon sign" displaying desired information is achieved. Three-dimensional lighted signage is believed to be more noticeable and appealing than two-dimensional signage. It is, therefore, a better medium for advertising and why neon signage is so prevalent.

25 Traditionally, there have been two ways to make three-dimensional lighted signs. In the case of "Neon", glass tubing is bent into the desired shape of the characters to be illuminated, the tubes filled with a fluorescent gas and a high voltage arc passed through it. The second method is to back-light a clear or opaque molded sheet of plastics material, wherein most of the background except the figures through
30 which light is to emerge is blacked out. In this latter method a mold is made over which a heated thermoplastic sheet is drawn. The sheet holds its shape upon cooling and can then be painted or printed with both light blocking and transparent inks and paints.

35 However, both of the aforesaid products suffer from being very time consuming to manufacture and are not easy or flexible to produce.

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Recently, there has been a move to manufacture illuminated signs that do not require the use of neon or other gases through which electricity is passed. One development is the manufacture of such signs using an ultra-violet curable, adhesive composition in the form of a gel applied to a base or substrate, such as a sheet of a clear acrylate, polycarbonate, glass, most common metals, thermoplastics and thermoset materials. The base may be overlaid with a vinyl material or screen printed, with clear areas known as "light channels" left uncovered until the curable, adhesive gel is applied thereafter and subsequently cured. When these signs are lit by normal light e.g. a fluorescent light, from the rear, the light is transmitted through the cured, adhesive gel and seen. The gel is preferably coloured and accordingly, the light transmitted from the gel is also of that colour. The adhesive gel on the sign is generally cured in a semi-cylindrical form on the substrate, which gives the transmitted light an apparent three-dimensional characteristic and the sign a look like a typical "neon sign". Different effects and characteristics may be achieved using different pigments in the adhesive gel and with different substrates.

The curable, adhesive gel generally is made having the consistency of toothpaste so that when applied to the substrate and allowed to cure, it retains the aforementioned generally semi-cylindrical shape thereon. In order to achieve this toothpaste consistency, the viscosity and thixotropy of the curable adhesive generally must be increased by the addition of inert fillers. Unfortunately, this addition of inert fillers normally entrains undesirable visible air bubbles into the adhesive. Since the cured, adhesive gel is to have light transmitted through it, it is most desirable that the cured adhesive composition be essentially free of visible air bubbles since the light transmitted through the cured gel will be refracted by the air bubbles and make the sign less attractive. It will be understood that "visible" bubbles, other than air bubbles, such as water vapour or mixed fluid bubbles also produce an inferior product.

The curable, adhesive gel compositions of the prior art made for the purpose of illuminated signs comprise photoinitiators to cause the gel to cure upon exposure to ultra-violet light. Ultra-violet curable, acrylic adhesive gels are essentially polymerizable reactive monomers and oligomers that are inhibited from premature curing, typically, by the presence of suitable inhibitors. Once the photo inhibitors are activated, preferably by exposure to ultra-violet light, the curable, gels polymerize into

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a cured, solid plastics material form. Other known conditions instead of exposure to ultra-violet light can also bring about polymerization. For example, high shearing during the mixing process in the manufacture of the compositions may cause polymerization. It has also been found that significant de-airing of the curable, adhesive gel composition may cause polymerization. Thus, the prior art teaches that the latter two conditions of high shearing or de-airing are to be avoided if premature, unwanted polymerization of the adhesive gel is to be prevented.

Air bubbles entrained into the curable adhesive gel during the addition of inert fillers would normally be removed by the use of vacuum means. However, vacuum degassing not only removes the large, visible air bubbles from the adhesive, but also, detrimentally, removes substantially all air, i.e., including desirable oxygen, to cause a reduction in the efficacy of the air-stabilized inhibitors in the curable, adhesive mixture. This either causes the adhesive to commence significant polymerization, immediately, or a slower, but effective polymerization to cause a substantial reduction in the shelf life of the curable adhesive composition.

Organopolysiloxane compositions, especially RTV (Room Temperature Vulcanizing) silicones are known in the art, see for example, USP 3474064 P. Hittmair et.al. issued October 21, 1969; USP 3491165 - K. Seyfried et. al. issued January 20, 1970; USP 3532664 - A.H. Smith, issued October 6, 1970; USP 5107008 - A. Ravis et. al. issued April 21, 1992; and USP 5247046 - Takayo et al. issued September 21, 1993. However, the methods of preparation according to the present invention of prior art RTV silicones provide improved curable silicone compositions having beneficial properties for the light sign utility hereinabove discussed. Thus, the invention is not limited to only those compositions exemplified, hereinafter, for the utility described but to all bubble-free adhesive compositions capable of being prepared by methods according to the invention suitable upon being cured for lighted sign use, as would be readily determined by the skilled artisan.

It is known that in order to cure an ultra-violet (UV) curable monomer or oligomer, the ultra-violet light must be able to penetrate through all levels of the composition with sufficient energy to initiate the polymerization reaction. This means that (1) the pigments used to colour the cured composition must allow sufficient UV light to pass through the curable composition, which sets an upper limit on the amount

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of pigment that can be used, and (2) UV light blockers and absorbers cannot be present in the required amounts sufficient to protect the pigments or polymers in the cured composition from the degenerating effects of UV exposure since too much pigment or UV light blocking compound(s) will inhibit the subsequent, desired complete curing of the polymer.

It is also known that pigment colour lightfastness when the composition is exposed to the elements of heat and UV radiation, depends upon the stability of the pigment and composition. The more exposure a pigment has to heat and UV radiation the faster it will degrade. Fluorescent pigments are especially susceptible to photolysis and autodegradation, and when used indoors tend to fade under constant bombardment from fluorescent lighting. UV blockers are, thus, typically, used to cover the light source and applied to the sign panel after the composition has cured, in order to extend the life expectancy. Lightfast pigments have been used for the outdoor versions of prior art compositions but they fade under the intense radiation and heat from the sun.

There thus remains a need for improved, non-neon light signs having visible bubble-free, cured polymer materials.

There also remains a need for improved non-neon light signs containing cured polymer materials, having improved light, particularly sunlight stability, which offers improved outdoor usage.

SUMMARY OF THE INVENTION

It is an object of one aspect of the present invention to provide a method of preparing an ultra-violet curable, adhesive gel composition that is light transparent and substantially free of visible air-bubbles, but that nevertheless contains sufficient air to prevent undesirable deactivation of UV inhibitors.

It is an object of a further aspect of the present invention to provide a method of preparing a light transparent curable, bubble-free adhesive gel composition for use in providing an improved cured product for exterior sign usage.

The present invention, thus, in one aspect relates to methods for preparing curable, adhesive gels intended to be used in sign-making. The adhesive gel is free of visible air, moisture or other bubbles which if present after curing of the gel would enhance the amount of the incidence of refraction of the light transmitted there

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through. The adhesive gel in the case of UV curable compositions should, however, have sufficiently trapped air to provide enough oxygen to interact with any inhibitors that may be present to inhibit polymerization until the adhesive gel is intentionally exposed to ultra-violet light.

5 Accordingly, in its broadest aspect, the invention provides a method for the preparation and storage of a light transparent, visible bubble-free homogenous, curable, adhesive composition for use in the manufacture of illuminated signs, said composition comprising a curable, adhesive compound and an inert filler, said method comprising the steps of:

- 10 (a) mixing under low shear conditions an effective amount of powdered said inert filler into said curable adhesive compound to provide a mixed curable, adhesive composition of desired viscosity and thixotropy;
- (b) treating said curable, adhesive composition to effect removal of substantially all visible bubbles therefrom to provide said bubble-free,
- 15 curable, adhesive composition; and
- (c) storing said bubble-free, curable, adhesive composition in substantially, fluid-tight containers.

 It is within the scope of this invention that a mixing step alone may constitute suitable mixing and treating of the admixture of filler and curable, adhesive

20 composition as hereinafter defined should no undesirable visible bubbles be present after the mixing step.

 Thus, the invention provides in a further aspect a process as hereinabove defined comprising mixing under low shear conditions an effective amount of powdered said inert filler into said curable adhesive compound to provide a mixed, curable,

25 adhesive composition of desired viscosity and thixotropy such that no visible bubbles are produced.

 By the term "low shear" in this specification and claims is meant those rates of shear which bring about satisfactory mixing of the components but which does not initiate premature polymerization of the curable monomers or oligomers of use in

30 the present invention.

 In one preferred aspect, the invention provides a method for the preparation of a light transparent, visible homogenous, curable, adhesive composition

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for use in the manufacture of illuminated signs, said composition comprising an inert filler and a curable, adhesive compound selected from a monomer and an oligomer, said method comprising the steps of:

- 5 (a) mixing under low shear conditions an effective amount of powdered said inert filler into said curable, adhesive compound to provide a mixed, curable, adhesive composition of desired viscosity and thixotropy;
- (b) spinning said mixed curable adhesive composition in a centrifuge at a spin rate and for a time period sufficient to substantially remove all visible air bubbles therefrom; and
- 10 (c) storing said spun curable, adhesive composition in a substantially air-tight and ultra-violet opaque container;

wherein said spin rate and said time period allow sufficient invisible air bubbles and absorbed air to remain in said spun adhesive composition to thereby provide suitable shelf life to said curable, adhesive composition prior to curing.

15 The invention provides in the method as hereinabove defined that said monomer and said oligomer are UV light curable; said composition further comprises an effective amount of an inhibitor for inhibiting premature curing of said monomer and oligomers; and an effective amount of a photoinitiator for effecting desired curing of said monomer and oligomer when exposed to ultra-violet light.

20 In a further aspect, the invention provides a light sign comprising a substrate having a portion defining a light channel, said light channel having adhered thereto a visible bubble-free and homogenous curable, adhesive composition prepared by a method as hereinabove defined. In yet a further aspect, the invention provides a light sign as hereinabove defined wherein said curable, adhesive composition has been
25 cured.

I have found that the most preferred inert filler to enhance viscosity and thixotropy is amorphous fumed silica in an amount of 5-20% w/w. While not being bound by theory it is believed that air is beneficially entrained and entrapped in the silica filler of the curable composition.

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As referred to hereinabove, the use of adhesive gels in sign-making requires that the gels have a consistency similar to that of toothpaste. Thus, inert fillers must be added to the adhesive mixture to increase the mixture's viscosity and thixotropy.

5 The method of the present invention provides that the adhesive compounds, particularly the UV curable compositions are prepared by mixing the oligomers, monomers, photoinitiators and inhibitors under low shear conditions. The inert filler, is added to the mixture during the low shear mixing step until the filler, most preferably, fumed silica has been completely wetted by the other components of
10 the mixture. It has been found that mixing under low shear conditions, as opposed to high shear conditions, reduces the likelihood of polymerization occurring.

 The addition and mixing of inert filler, particularly amorphous fumed silica, to the mixture results in air bubbles being entrained and entrapped in the mixture. Because of the relatively high viscosity and thixotropy of the adhesive
15 compound, it is believed the entrained invisible air bubbles remain trapped within the adhesive compound. According to the method of the present invention, the larger, visible air bubbles are removed from the curable, adhesive composition by spinning of the composition in a centrifuge. The adhesive compound is spun at a spin rate and for
20 a time period sufficient to cause substantially all the visible air bubbles to be removed from the compound, while allowing sufficient air to remain in the compound. The remaining air provides oxygen that interacts with the inhibitors, thereby assisting in inhibiting polymerization of the reaction. This, in turn, provides increased shelf life to the adhesive compound as compared to an adhesive compound that has been degassed by vacuum means.

25 Thus, the present invention provides in one aspect a method for preparing an ultra-violet curable adhesive composition that is substantially free of visible air bubbles. The composition is spun in a centrifuge until all visible bubbles are removed, yet leaving sufficient air in the adhesive composition to assist in inhibiting polymerization.

30 In a more preferred aspect, the invention provides non-UV curable adhesive compositions comprising as base substrate a light transparent, curable, silicone polymer, preferably a room temperature vulcanizing (RTV) slightly opaque, fully

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Preferred inhibitors are selected from the group consisting of hydroquinone monomethylether and hydroquinone.

In a more preferred aspect the invention provides a method as hereinabove defined further comprising dispersing a pigment in said curable compound or composition; yet more preferably, prior to the spinning step if carried out.

In a non-UV curable composition of use in the present invention, the curable compound is a silicone.

Although not preferred, the invention includes compositions comprising free radical peroxide and persulphate curable monomer and oligomer adhesives.

In the case of preferred UV curable compositions of the invention monomer and oligomer acrylic adhesive compounds are present in admixture with polymerizable isocyanates, polyesters and olefines, such that the cured compound is comprised of a base material such as an acrylated urethane, acrylated epoxy or acrylated polyester. Acrylated urethane is the preferred base material obtained from the curable, acrylic adhesive.

Thus, the invention provides in one aspect a method as defined hereinabove, wherein said adhesive compound comprises a monomer or oligomer selected from a polymerizable acrylic acid, acrylate, methacrylate, isocyanate, polyester, polyol and epoxy resin, to provide on curing a curable polymer selected from the group consisting of an acrylated urethane, acrylated epoxy and acrylated polyester resin.

Photoinitiators are present in admixture with the adhesive composition to cause polymerization of the oligomers and monomers upon exposure to UV light. Inhibitors are also present in the adhesive to inhibit premature polymerization of the oligomers and monomers. The inhibitors are, therefore, intended to inhibit the polymerization reaction until the adhesive gel is actually exposed to UV light. The inhibitors, preferably hydroquinone monomethylether or hydroquinone, are thought to interact with any oxygen present in the adhesive gel to inhibit polymerization. It has been found that substantial degassing of the adhesive gel, particularly by vacuum degassing, results in the immediate onset of polymerization, or results in a relatively short shelf life of the adhesive gel. By shelf life it is meant the time during which the adhesive gel can be stored prior to unwanted polymerization occurring.

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transparent or translucent silicone polymer, optionally mixed with UV light blocking and absorbing agents, dyes, pigments and other fillers. The curable silicones are cured by hydrolysis with water in the form of moisture, steam and the like. The RTV silicones may be either neutral or acid catalysed curable silicone polymers. The cured compositions are used as optically brilliant three-dimensional signs and lettering for both interior and exterior use. To eliminate or prevent the presence of visible bubbles, either water or air, the curable silicone and filler compositions are preferably manufactured through the use of static mixers.

Preferred silicones of use in the present invention, for example, include, methyltrimethoxysilane, dimethylpolysilane and methyl dimethyl polydimethylsilane RTV resins.

The fillers comprise amorphous or hydrophobic fumed silica for viscosity and thixotropy control, UV blocking/absorbing agents, such as, for example TINUVIN® (Ciba-Geigy) and fluorescent and non-fluorescent inorganic and organic coloured pigments.

The curable silicone composition is compounded with the desired fillers in effective amounts to form the gel or paste by use of precision effective metering and static mixing under an inert, ultra-dry atmosphere and, similarly, stored in a fluid (air and moisture) tight container.

Preferred, curable compositions comprise RTV silicone adhesives. Most preferred RTV silicone compositions comprise mixtures of methyltrimethoxy silane (CAS# 1185-55-3), ME-Dimethoxy/STP Polydimethyl siloxane (CAS# 68037-58-1) and dimethylpolysiloxane (CAS# 63148-62-9), for example, provided under the RTV5810 series of silicone rubber sealants (General Electric Co.) which absorb water from the atmosphere to effect cure.

The pigment fillers are added, generally, as a dispersion of the organic or inorganic pigment in a silicone fluid containing, for example, 80-90% w/w dimethylpolysiloxane (CAS# 63148-62-9). Pigments of preferred use are known as "transparent" pigments because of their very small primary particle size and high degree of dispersion. The pigments may be of the fluorescent type dyes in a resin matrix ground into extremely fine particles. The pigment in the cured composition absorbs all of the wavelengths of light other than those wavelengths it reflects or

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transmits. Fluorescent pigments appear to amplify the light passing through the cured bead, possibly by conversion of UV light to a wavelength in the visible spectrum. Luminescence is often seen with such transparent pigments which causes the cured coloured bead to glow.

5 Although not necessary, even for outdoor use, the silicone composition of the invention may comprise UV blocking agents, such as of the hindered amine type known as HALS.

10 In further alternative aspects, the invention provides compositions prepared by methods as hereinabove defined, and three-dimensional beads comprising cured said compositions when cured on a substrate.

 A curable composition as hereinabove defined may be dispensed manually or most preferably using a computer controlled dispensing apparatus for highly repeatable reproductions according to the prior art.

15 **BRIEF DESCRIPTION OF THE DRAWINGS**

 In order that the invention may be better understood preferred embodiments will now be described by way of example only with reference to the accompanying drawings; wherein

20 Fig. 1 is a diagrammatic cross-sectional view, in part, of a light sign showing a raised bead printed on a substrate, wherein a light channel is formed by the application of a light blocking substance upon the underside of the substrate, in accordance with the present invention;

25 Fig. 2 is a diagrammatic cross-sectional view, in part, of a light sign showing a raised bead printed on a substrate wherein a light channel is formed by the application of a light blocking substance upon the topside of the substrate, in accordance with the present invention;

 Fig. 3 is a diagrammatic cross-section of a bead of cured material according to the invention;

30 Fig. 4 is a diagrammatic cross-section of a bead of cured material according to the prior art; and wherein the same numerals denote like parts.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

With reference to Figs. 1 and 2, these show, in part, an illuminated sign case shown generally as 10, having plastics frame side walls 12, a UV light source 14 and a sign front substrate 16 formed of a transparent polycarbonate.

In Fig 1, substrate 16 at its backside 18 has a light blocking film 20 adhered thereto or printed thereon. Film 20 may be a thermoplastic, a thermoset, a metal foil or a paint or ink. Film 20 has portions defining a light channel aperture 22 through which light passes to cured composition bead 24, adhered over light channel 22 to front side 26 of substrate 16.

The embodiment shown in Fig. 2 has no light blocking film 20 on backside 18 of substrate 16 but has such a film 28 on front side 26 of substrate 16. Film 28 has portions defining light channel 30 through which light from source 14 passes to bead 24.

Fig. 3 represents cured bead 24 having no visible bubbles, air or water, according to the invention. Light transmission through bead 24 is denoted by arrows 32.

Fig. 4 represents a cured bead 34 of the prior art having air bubbles 36 which diffract and absorb light as represented by arrows 38.

In a preferred embodiment of the method of the present invention, the mixed adhesive compound is spun in a centrifuge at a spin rate in the range of about 2500 rpm to about 6000 rpm. Preferably, the spin rate is between about 3000 rpm and about 4500 rpm, and most preferably 4000 rpm. The time period during which the mixed adhesive composition is spun in order to provide the desired adhesive composition is inversely related to the spin rate. That is, the faster the spin rate, the smaller the time period. The spin rate and time period are selected to remove substantially all visible air bubbles from the adhesive composition, while leaving enough invisible air to assist the inhibitors. As well, the spin rate and time should not cause the other individual components of the adhesive composition to separate. That is, spinning of the composition at too fast a spin rate or for too long causes the individual components to separate, based on their respective specific gravities. The result is a non-homogeneous mixture of the components.

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It has been found that satisfactory results are achieved if the mixed adhesive composition is spun for about 5 minutes at a spin rate of 3000 rpm and for about 1.5 minutes at a spin rate of 4500 rpm. Preferably, the mixed adhesive composition is spun for 2 minutes at a spin rate of 4000 rpm. It should be noted that the term "time-period" as used herein refers to the total time that the composition is spun, including the initial accelerating phase of the centrifuge and the final deceleration phase. Thus, for example, at the preferred spin rate of 4000 rpm, the composition is spun for a total time period of about 2 minutes, in which about 100 seconds are at the actual spin rate of 4000 rpm.

I have also found that the mixed, curable, adhesive composition most preferably should be spun at an angle substantially horizontal, i.e. perpendicular to the axis of rotation. Deviation from this horizontal rotational plane does not provide visible air bubble removal, due to adhesion thereof to the sides of the centrifuge tubes holding the composition.

It has been found that using the method of the present invention, the shelf life of cured acrylic adhesive composition is about 6 months, and can in some cases be a lot longer. This is comparable to a shelf life of about 1 1/2 months in the case of the acrylic adhesive compositions degassed by vacuum, although the adhesive composition may polymerize during, or shortly after, such vacuum degassing.

In a preferred embodiment of the method of the present invention, a pigment to provide colour to the adhesive compound is dispersed within the compound prior to the mixing step. Any suitable pigment may be used to provide the desired colour to the compound.

The method of the present invention may be carried out as follows, although it is understood that the present invention is not limited to the particular conditions described.

Typically, a 300 pound batch of UV light curable, acrylic adhesive composition is made at one time. The monomer, oligomer, photoinitiator and inhibitor components are placed in a bottom-ported plastic barrel and mixed using a low shear helical mixer until the components are thoroughly blended. A pigment, if used, is added to the liquid components prior to mixing. The inert filler, preferably amorphous fumed silica, is added while the liquid components are continuously agitated. The inert

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filler makes up between about 5% and about 15% by weight of the total adhesive composition, and preferably 10% by weight if amorphous fumed silica is used.

5 The mixture is further mixed under low shear conditions until homogenous. The barrel is then capped and placed on a roller, on which the barrel is rolled at a rate of about 6 inches per second, as measured on the outside diameter of the barrel. After 12 hours of rolling, the barrel is taken off the roller and the adhesive composition mechanically mixed with a helical mixer until all the composition has been repositioned in the barrel. The barrel is then recapped and rolled for another 12 hour period, during which time the composition becomes uniform in the barrel, and builds
10 in viscosity and thixotropy.

After the second twelve hour rolling period, the rheological characteristics of the mixed adhesive composition are tested. Preferably, the viscosity of the adhesive composition will be in the range of about 100,000 centipoises to about 800,000 centipoises, as measured using a spindle number 7 at 2.5 rpm on a Brookfield
15 DV-1 viscometer. The thixotropy of the adhesive composition is measured on a flow test jig. In a three minute test, the distance the sample travels should, preferably, be between 2.5 and 5.75 centimetres.

If the rheological characteristics of the mixed adhesive compositions are acceptable, the composition is then loaded into cartridges through a mandrel fastened
20 to a positive displacement pump affixed to the bottom of the barrel. The cartridges are, preferably, opaque to ultra-violet light to prevent accidental polymerization of the composition. Any large, visible air bubbles that were entrained and entrapped into the adhesive compound during the mixing and pumping stages are separated by spinning the cartridges in a centrifuge.

25 The cartridges are placed into supportive retainer sleeves. The sleeves are placed into trunnion rings which are attached to the rotor of the centrifuge. When the rotor spins, the retainers swing outward to a horizontal position with the plugged ends of the cartridges furthest away from the rotor and the open ends closest to the rotor, i.e. perpendicular to the axis of rotation. The adhesive composition in the
30 cartridges becomes stratified by specific gravity. The heaviest parts (fluids) are forced furthest from the rotor while the lighter air bubbles move closer to the rotor until they are separated from the fluid altogether. If the composition is spun too long or too fast,

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the fluid components will start to separate. It has been determined that the optimal time is about 100 second at a speed of 4000 rpm. These conditions separate the visible air bubbles from the fluid without separating the fluid itself.

After spinning, plungers are inserted into the cartridges. These plungers
5 are transparent and do not have wiper seals so as to minimize the opportunity to further trap air bubbles during plunging and to be able to see any inadvertently entrapped air. A custom designed plunging machine "walks" the plunger into the cartridge and displaces any air trapped under the plunger up the side of the plunger, and out of the back of the cartridge. The plunging machine also ensures an occlusive seal around the
10 plunger so the plunger will not move during shipping and handling. The excess composition behind the plunger is removed and the cartridge is labelled and shipped.

In the process according to the invention wherein the inert filler and visible, bubble-free, curable compositions are mixed, such as not to form visible bubbles under low shear, a static mixing process is most preferred. The resulting
15 curable composition from the motionless static mixer is dispensed through a mandrel directly into an ultra-dry nitrogen purged cartridge sealed at the outlet end. The cartridge is removed from the mandrel and the back of the cartridge is purged with ultra-dry nitrogen. The cartridge plunger is pushed into the cartridge while the cartridge is deformed until all of the gas between the plunger and the curable adhesive
20 composition has been exhausted. This ensures an air and moisture tight seal.

Alternatively, the cartridge may be filled from the outlet end, whereby, prior to filling, the plunger is inserted and bottomed out in the cartridge. The outlet of the cartridge is purged with ultra-dry nitrogen and is coupled to the outlet of the meter-mix machine. As the composition is dispensed from the meter-mix machine it is
25 injected into the cartridge and pushes the plunger back. When full, the cartridge is removed from the meter-mix machine and a tip cap is inserted to seal it.

Alternatively, the printing composition of the invention can be dispensed directly from the same meter-mix into a larger container such as a one gallon pail, or a five gallon pail, or a twenty litre pail, or a forty-five gallon drum, or a 200 litre
30 drum or similar, the main considerations being that it is first purged with ultra-dry nitrogen, that it is impervious to moisture penetration and there are facilities available to remove the printing composition from said container without introducing air or

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contaminating it with water or any foreign debris. It must also seal completely and be chemically compatible with the printing composition.

5 Alternatively, the printing composition may be packaged directly from the meter-mix machine into a collapsible package such as a toothpaste type tube or bag or any other format that can keep it from being contaminated by water from which it can be dispensed. In the case of moisture-curable silicone monomers and polymers, the package must be ultra-dry nitrogen purged before filling and prior to sealing in any case.

10 A preferred method of applying the curable bubble-free compositions of the invention to a substitute for curing thereon to provide the cured three-dimensional sign or lettering, is by use of computer controlled dispensing machine of the type produced by Luminart Inc, Mississauga, Ontario, Canada or Camelot Systems Inc., Haverhill, Mass., U.S.A.

15 In operation, the curable printing composition is loaded into cartridges, each cartridge having a hole at one end to accommodate a dispensing needle. the dispensing needles can be of different shapes and sizes. At the opposite end of the cartridge is a plunger which fits snugly within the internal diameter of the cartridge. The plunger can move the entire length of the cartridge. When the cartridge is filled with the printing composition the plunger is installed and makes intimate contact with the printing composition trapping it between the plunger and the outlet.

20 The cartridges are loaded into a form fitted retainer which is attached to the moveable arm of the dispensing machine. The retainer is orientated in a holder which holds it straight up and down with the outlet of the cartridge at the bottom. The retainer is fitted to a switched compressed air outlet by means of a length of tubing. When the switch is turned on, regulated compressed air enters the retainer and pressurizes it. The compressed air advances the plunger in the cartridge displacing the printed composition through the outlet.

25 To make a sign, the operator programs the path along which the printing composition is applied, teaching the machine the coordinates of each point along the path and giving it instructions as to how high the retainer should be held at each point and whether or not a compressed air switch should be opened or closed. In the "Run" mode, the dispensing machine retraces the programmed path with the retainer at the

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proper height, opening the compressed air switch, pressurizing the retainer and displacing the printing composition at the beginning and during the length of each line, and closing the airswitch and de-pressurizing the retainer, stopping the displacement at the end of each line. At the end of each line the retainer lifts relative to its dispensing height.

Alternatively, rather than dispensing from a cartridge, the printing composition may be fed to a valved dispensing apparatus from a larger reservoir such as a one gallon pail, or a five gallon pail, or a twenty litre pail, or a forty-five gallon drum, or a 200 litre drum or similar. The outlet of this apparatus will be affixed to the moveable arm of the dispensing machine which will tell it when to open and close. When open, this apparatus will allow a constant stream of printing composition to flow upon the substrate in the form of a bead. When closed, the dispensing will cease and the bead of the printing composition will end.

A sign is created with one or many of these beads applied over light channels.

Before, during and after manufacturing, the components and finished printing composition are maintained in an inert moisture-free environment, prior to curing. After the printing composition 11 has been applied to substrate 12, it is placed in a dust-free, ambient environment where it polymerizes through the absorption of water primarily from the atmosphere.

Alternatively, it can be placed in a chamber which incorporates higher levels of heat and humidity to speed up the polymerization process.

The curable, adhesive composition after application to the lighted sign substrate may be cured by the application of UV light, if UV light curable; or by water if curably sensitive thereto.

Example 1

Table 1

Table 1 gives examples of UV-curable formulations comprising acrylic based compositions and, optionally, a pigment in the amounts stated, hereinbelow.

- 17 -

Component	A (% w/w)	B (% w/w)	C (% w/w)	D (% w/w)	E (% w/w)
Acrylated oligomer ¹	32.5	40	45	48.2	40
1,6 Hexanediol diacrylate	20	24	20.2	30	15
N-vinyl Pyrrolidinone ²	17.5	4.3	4.3	-	18.3
2-Ethoxy-ethoxy-ethylacrylate ³	17.5	17	17.5	8.7	18.3
2-hydroxy-2methyl 1-phenyl -propane -1-one ⁴	3	2.6	3.5	3.5	3.6
Hydrophobic fumed silica ⁵	9.5	9.5	9.5	-	4.8
Amorphous fumed silica ⁶	-	-	-	9.2	-

Key

- 15-1512 Acrylated oligomer (McWhorter):
alkanedioic acid, polymer with a-hydroxy-w-hydroxypoly (oxy-1,4, butanediyl), 5-isocyanato-1-(isocyanomethy)-1,3,3-trimethylcuclyhexane and mixed alkonols, 2-hydroxy ethyl acrylate blocked (urethane-acrylate polymer)
- V-PYROL, RC (ISP TECHNOLOGIES)
- SR256 (SARTOMER)
- DARDOCUR 1173 photoinitiater (CIBY-GEIGY)
- R972 (DEGUSSA)
- AEROSIL 300 (DEGUSSA)

The above compositions were used as base curable formulations in admixture with suitable pigments as follows in either (a) back lit, or (b) front lit systems.

FIRE RED - (STERLING 920-21) 5 parts: 95 parts composition A(b)

OLYMPIC BLUE - (STERLING B10-70) 4 parts: 96 parts composition B(b)

WARM ORANGE - (LANTER TS13) 2.5 parts: 97.5 parts composition E(a)

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GLOSS WHITE - (HOECHST 01-DUE-27) 0.5 parts: 99.5 parts composition C(a)
 CANARY YELLOW - (DAYGLO Z-16-3) 0.03 99.97 parts composition D(a)

The component parts were combined in a "Ross Versamix" low shear mixer. The silica component was added last because it was most difficult to entrain. Once the full amount of silica was wetted out, the mixer was activated in the mixer for about 2 hours. The high speed dispersion blade was run at about 100 RPM and the Anchor blade assembly was run at about 200 RPM. At the end of the cycle, a sample was taken and tested for thixotropy and flow characteristics. When it passed inspection, the batch was mixed under 30" hg vacuum for 3-5 minutes. The mixed composition was then pressed out of the mixing vessel through its bottom port through a stainless steel strainer into a cartridge mandrel filler. A cartridge was filled to a weight of 189 grams of curable composition and spun in a centrifuge such that the tip of the cartridge was subjected to 4,000 gravities for four minutes. After spinning, the cartridge was removed from the centrifuge and visually inspected to be air bubble-free. A sealess plunger was placed in the cartridge to provide an air-tight seal.

Example 2

Table 2 gives examples of moisture curable RTV silicone adhesive compositions based on RTV5810 series (General Electric Silicones), comprising mixtures of methyltrimethoxysilane, methyl dimethoxy/STP polydimethyl siloxane and dimethyl polysiloxane resins.

TABLE 2

	<u>Parts</u>	<u>Percentage</u>
25	Pink	
	100 Sil	90.9
	9.5 H9502 (HCC19466 & A 21)	8.636
	0.5 A 300	0.455
30	110 PARTS	100%
35	Fire Red	
	100 Sil	90.9
	7.308 H9502 (HCC19466 & A 21)	6.644
	0.385 A300	0.35
	2.308 T 171	2.098
	110 PARTS	100%

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5	Olympic Blue	100 Sil	90.9
		7.746 DC 200	7.042
		0.399 A 300	0.363
		0.176 H9502 (HCC 19466 & A21)	<u>0.159</u>
		110 PARTS	100%
10	Gloss White	100 Sil	90.9
		6.249 DC 200	5.681
		0.322 A300	0.293
		0.141 H9502 (HCC19466 & A21)	0.128
		1.974 T171	1.795
		<u>1.33 T292</u>	<u>1.209</u>
		110 PARTS	100%
15	Canary Yellow	100 Sil	90.9
		9.21 DC 200	8.372
		0.475 A 300	0.431
		<u>0.209 STANTONE RED</u>	<u>0.19</u>
		110 PARTS	100%
20	Warm Orange	100 Sil	90.9
		7.164 DC 200	6.513
		0.368 A 300	0.335
		0.162 STANTONE RED	0.147
		<u>2.328 T 171</u>	<u>2.116</u>
		110 PARTS	100%

			<u>% W/W</u>
30	Wherein Sil is RTV5818:		
	Methyltrimethoxysilane (CAS #1185-55-3)		1 - 5
	Methyldimethoxy/STP Polydimethyl-siloxane (CAS #68037-58-1)		60 - 80
	Dimethylpolysiloxane (CAS #63148-62-9)		10 - 30
35	and		
40	DC 200	- OCTAMETHYLTRISILOXANE, DOW CORNING 200	
	A 300'	- AMORPHOUS FUMED SILICA	
		- AEROSIL 300	
45	STANTONE RED	- SILICONE FLUID CONTAINING 80-90%	
		DIMETHYLPOLYSILOXANES CAS # 63148-62-9	
		- QUINACRIDONE CI PIGMENT VIOLET 19, CL #46500	
		- STANTONE 235P04 RED	

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T 292 - BIS (1,2,2,6,6 - PENTAMETHYL - 4 - PIPERIDINYL)
 SEBACAE
 - TINUVIN 292

5 T 171 - (2-h-BENZOTRIAZOL-2-YL)-4-METHYL-6-
 DODECYLPHENOL

 Sil RTV5810

10 A moisture RTV curable silicone composition was made as follows:

 16 parts of Dayglo ® Corona Magenta part number A-21, 12 parts of
Ciba Geigy's Tinuvin 292 ® Hindered Amine Light Stabilizer, 18 parts Tinuvin 171
Ultra Violet Light Absorber, and 3 parts of Degussa's Aerosil 300 ® amorphous fumed
15 silica in 51 parts dimethylepoysiloxane fluid (CAS# 63148-62-9), were mixed using a
three-roll mill or a "Ross Powermix" disperser. This dispersion was degassed until all
visible air was stripped from it. It was then transferred to an ultra-dry nitrogen purged
reservoir where it was blanketed with ultra-dry nitrogen gas. The reservoir was then
attached to a two-pump volumetric metering machine. The other pump was attached
20 to a reservoir which had also been ultra-dry nitrogen purged and loaded with RTV 5818
single component, unpolymerized silicone rubber composition. The dispersion and
RTV silicone rubber composition were metered in the ratio of 1 part dispersion to 10
parts RTV Rubber composition and dispensed through a static mixer. The size and
number of elements in the mixer may vary, but best mixing results were obtained using
25 a "Combination" static mixer. The 12 beginning elements in this mixer are 1.3 cm.
in diameter in a 1.3 cm. inside diameter housing followed by a 2.0 cm. diameter
housing, in which there are 26 elements 2.0 cm. in diameter. The section between the
two different sized elements is about 7.5 cm. long where there are no elements. The
diameter of the housing at this point is 7.5 cm.. The combined silicone rubber
30 compound and dispersion were presented to the large diameter mixing elements,
simultaneously, in the aforesaid ratio. The components pass by the elements to
combine split and recombine effectively layering the two compositions in the housing
in a multitude of layers. At the end of the elements, the housing restricts to 7.5 cm
inches in diameter. There is a section about 7.5 cm. long having no elements. The
35 components proceed through this section to a second group of 26 elements which are

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EXAMPLE 3

This example describes a typical bubble-free curable epoxy adhesive composition of use in the present invention.

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Part "A"	Parts Per Hundred
Epoxy Resin	68
Aliphatic Glycidyl Ether	23
Amorphous Fumed Silica	9
Part "B"	Parts Per Hundred
N-Aminoethylpiperazine	18
Triethanolamine	13.5
Amido-amine Resin	13.5
Diethylenetriamine	9
Nonylphenol	6
Triethylenetriamine	9
Aliphatic Glycidyl Ether	6
Bisphenol "A"	6
Piperazine	5
Diamine	3
Amorphous Fumed Silica	9
Bis (12266 - pentamethyl-4-piperidinyl) sebacate	1
Hydrophenylbenzotriazole	1

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smaller in diameter than the first elements, where they were again divided reoriented and recombined at each element to form more layers until the compositions were completely blended. The number of layers formed at the outlet of this mixer is 2 to 38th power. The pumps are sized such that given the pressure drop of the mixer and the high viscosity of the composition, the flow rate at the outlet is about 400 grams per minute. At the end of the mixer is a mandrel whose outside diameter approximates the internal diameter of the cartridge in which the mixed bubble free curable composition was packaged. A cartridge was ultra-dry nitrogen purged, placed over the mandrel and an aliquot of composition taken into it. The cartridge was pushed off the mandrel by the fluid being injected into it. At the completion of the metered shot, the cartridge was removed completely from the mandrel, the exposed composition ultra-dry nitrogen purged and a plunger inserted to seal off the back end of the cartridge. Alternatively, the composition was dispensed directly from the static mixer into a pail or drum which had been dried and nitrogen purged before and after the filling operation. A sealing cap was placed on it, immediately.

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On admixture, 4 parts of "A" were mixed with 4 parts of "B".

Preparation:

The components of Part "A" and Part "B" were mixed together under high shear and vacuum to eliminate entrapped air and then loaded bubble-free into a meter-mix-dispense device. They were metered in the ratio of 4 parts of Part "A" to 1 part of Part "B", with both streams being introduced, simultaneously, into a static mixer. The outlet of the static mixer was connected either to the cartridge filling device or directly into an X-Y-Z dispenser. The viscosity and thixotropy of the composition were sufficient to keep it from slumping on the sign substrate once it has been applied until curing took place. This composition was a thermoset resin and began to polymerize within 0.5-2 hours after the two components were brought together.

EXAMPLE 4

This example illustrates a pre-urethane polymer formulation of use in the present invention.

Part "A"	Parts Per Hundred
Polyether Polyol	87
Polysiloxane	3
Hydrophobic Amorphous Fumed Silica	10
Part "B"	Parts Per Hundred
Dicyclohexylmethane -4,4- Diisocyanate	70
Diphenylmethane Diisocyanate	18
Phenyl Isocyanate	1
Hydrophobic Amorphous Fumed Silica	10
Bis (12266 - pentamethyl -4-piperidinyl) sebacate	0.5
Hydrophenylbenzotriazole	0.5

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5 The components of Part "A" over Part "B" were mixed together in an ultra-dry nitrogen environment under high shear until the parts were thoroughly blended. The compositions were then degassed at 760 mm Hg vacuum for 15 minutes while being agitated to eliminate entrapped gas. Parts "A" and "B" were then loaded
10 bubble-free into a dried meter-mix-dispense device. Extreme care was taken to avoid contaminating either part, but especially Part "B", with moisture. They were metered in the ratio of 1 part of Part "A", to 1 part of Part "B", while both streams being introduced simultaneously in a static mixer. The outlet of the static mixer was connected either to the cartridge filling device or directly onto an X-Y-Z dispenser.
15 The viscosity and thixotropy of the composition were sufficient to keep it from slumping on the substrate once it had been applied until curing occurred.

15 Although the disclosure describes and illustrates certain preferred embodiments of the invention, it is to be understood that the invention is not limited to these particular embodiments. Rather, the invention includes all embodiments which are functional equivalents of the specific embodiments and features described and illustrated.

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1. A method for the preparation and storage of a light transparent, visible bubble-free homogeneous, curable adhesive composition for use in the manufacture of illuminated signs, said composition comprising a curable, adhesive compound and an inert filler, said method comprising the steps of:

- (a) mixing under low shear conditions an effective amount of powdered inert filler into said curable, adhesive compound to provide a mixed curable, adhesive composition of desired viscosity and thixotropy;
- (b) treating said curable, adhesive composition to effect removal of substantially all visible bubbles therefrom to provide said bubble free, curable adhesive composition; and
- (c) storing said bubble-free, curable adhesive composition in substantially, fluid-tight containers.

2. A method as defined in claim 1 for the preparation of a visible light transparent, air-bubble-free, homogeneous, curable, adhesive composition wherein said curable, adhesive compound is selected from a monomer and an oligomer, said method comprising the steps of:

- (a) mixing under low shear conditions an effective amount of powdered inert filler into said curable, adhesive compound to provide a mixed curable, adhesive composition of desired viscosity and thixotropy;
- (b) spinning said mixed, curable, adhesive composition in a centrifuge at a spin rate and for a time period sufficient to substantially remove all visible air bubbles therefrom to provide a visible air bubble-free and homogeneous, curable, adhesive composition; and
- (c) storing said spun, visible air bubble-free, curable adhesive composition in a substantially air-tight and ultra-violet opaque container; wherein said spin rate and said time period allow sufficient invisible air bubbles and absorbed air to remain in said spun adhesive composition to thereby provide suitable shelf life to said curable, adhesive composition prior to curing.

3. A method as defined in claim 1 wherein said mixing under low shear conditions

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said effective amount of powdered inert filler into said curable, adhesive compound to provide said mixed, curable, adhesive composition of desired viscosity and thixotropy is such that no visible bubbles are produced.

4. A method as defined in claim 2 wherein said monomer and said oligomer are ultra-violet light curable; said composition further comprising an effective amount of an initiator for inhibiting premature curing of said monomer and said oligomer until exposed to ultra-violet light; and an effective amount of a photoinitiator.

5. A method as defined in claim 1 wherein said inert filler is selected from amorphous silica and fumed silica and is present at a concentration of 3 to 15% w/w in said curable, adhesive composition.

6. A method as defined in claim 5 wherein said silica is at a concentration of 8 - 20% w/w in said curable, adhesive composition.

7. A method as defined in claim 2 further comprising dispensing a pigment in said curable, adhesive compound in said mixing step.

8. A method as defined in claim 1 wherein said mixing under low shear conditions step is effected comprising static mixing conditions.

9. A method as defined in claim 1 wherein said mixing under low shear conditions step comprises rolling of said mixed adhesive composition.

10. A method as defined in claim 1 wherein said mixture is spun at an angle substantially horizontal.

11. A method as defined in claim 1 wherein said composition further comprises an effective amount of an ultra-violet light stabilizer.

12. A method as defined in claim 1 wherein said compound comprises a RTV adhesive silicone.

13. A method as defined in claim 11 wherein said RTV adhesive silicone is selected from the group consisting of methyl trimethoxysilicone, methyldimethoxy/STP polydimethyl siloxane and dimethylpolysiloxane.

14. A method as defined in claim 12 wherein said bubble-free curable adhesive composition comprises 1-5% w/w methyltrimethoxysilane (CAS No. 1185-55-3), 60-80% w/w methyldimethoxy/STP polydimethyl-siloxane (CAS No. 68037-58-1) and 10-30% W/W (CAS No. 63148-62-9).

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15. A method as defined in claim 1, wherein said adhesive compound comprises a monomer or oligomer selected from a polymerizable acrylic acid, acrylate, methacrylate isocyanate, polyester, polyol and epoxy resin to provide on curing a curable polymer selected from the group consisting of an acrylated urethane, acrylated epoxy and acrylated polyester resin.

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16. A method as defined in claim 15 wherein said cured polymer is an acrylated urethane.

17. A light sign comprising a substrate having a portion defining a light channel said light channel having adhered thereto a light transparent, visible bubble-free, curable, adhesive composition prepared by a method as defined in Claim 1.

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18. A light sign as defined in Claim 17 when said curable, adhesive composition has been cured to provide a flexible material.

19. A light sign as defined in Claim 18 wherein said flexible, curable, adhesive composition has been cured by the action of water.

15

20. A light sign as defined in Claim 18 wherein said flexible, curable, adhesive composition has been cured by the action of UV light.

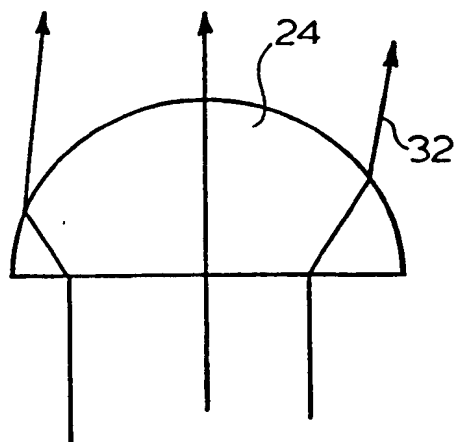
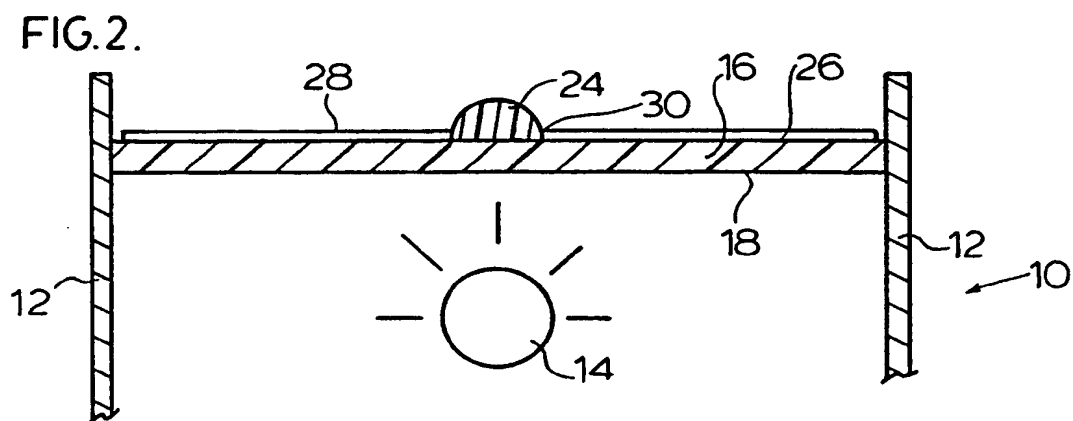
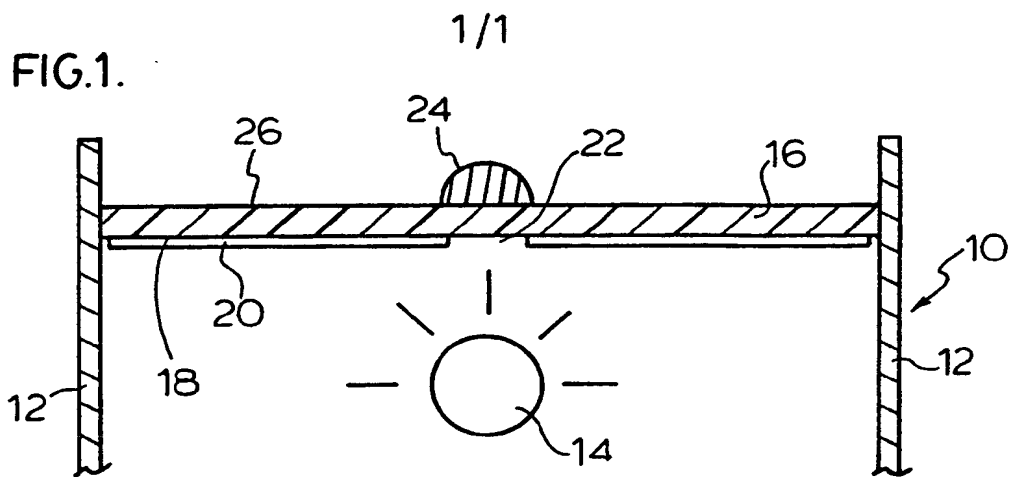


FIG.3.

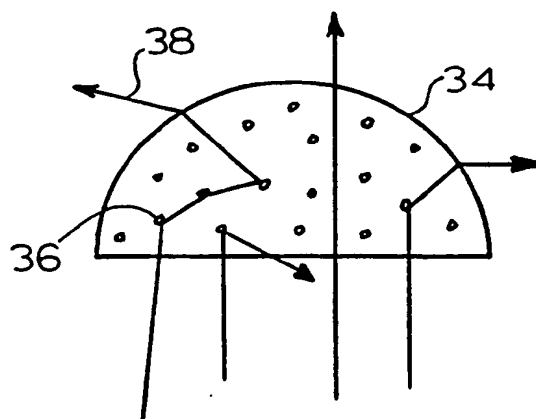


FIG.4. PRIOR ART

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/CA 95/00153

A. CLASSIFICATION OF SUBJECT MATTER

C 09 J 9/00

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 09 J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A, 92/02 306 (LOCTITE CORPORATION) 20 February 1992 (20.02.92), claims; page 1, line 1 - page 4, line 30. --	1
X	DATABASE WPIL, no. 94-107037; & JP,A,06 057 221 (KANEKA CORP.) --	1
X	EP, A, 0 435 301 (VEREINIGTE ZIGARETTEN- FABRIKEN DRESDEN GMBH) 03 July 1991 (03.07.91), claims; example. --	1, 3
A	DD, A, 237 632 (INGENIEUR HOCHSCHULE	1, 2

☒ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search
26 June 1995

Date of mailing of the international search report

13. 07. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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PAMMINGER e.h.

INTERNATIONAL SEARCH REPORT

-2-

International Application No
PCT/CA 95/00153

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>MITTWEIDA) 23 July 1986 (23.07.86), claim; example. -----</p>	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/CA 95/00153 SAE 106282

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
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La présente annexe indique les
membres de la famille de brevets
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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
WD A1 9202306	20-02-92	AT E 112187 DE C0 69104367 DE T2 69104367 EP A1 542783 EP B1 542783 IT A0 9021102 IT A 1243378 JP T2 5508817	15-10-94 03-11-94 16-02-95 26-05-93 28-09-94 27-07-90 10-06-94 09-12-93
EP A2 435301	03-07-91	DE C0 59008084 EP A3 435301 EP B1 435301 HU A0 908461 HU A2 57561 TR A 26378	02-02-95 11-12-91 21-12-94 29-07-91 30-12-91 15-03-95
DD A1 237632	23-07-86	keine - none - rien	

